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**TECHNICAL REPORT ARAED-TR-87022** 

# ORGANIC COATINGS TO IMPROVE THE STORAGEABILITY AND SAFETY OF PYROTECHNIC COMPOSITIONS

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# **NOVEMBER 1967**



U. S. MONY MONOMENT RESERVOK, DEVELOPMENT AND ENGINEERING CENTER

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# INTRODUCTION

One of the most perplexing problems facing engineers and scientists developing decoy flares is how to prevent the reaction of finely divided mangnesium (Mg) ( $\simeq 23$  micron diameter) with water under storage conditions. This reaction reduces the surface reactivity of the Mg with the concomitant production of hydrogen (H<sub>2</sub>) by the following reaction:

$$Mg + 2H2O + Mg(OH)2 + H2 +$$

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Production of  $\rm H_2$  in systems having minimal free volume can result in pressures rupturing cases and seals. This reaction can also create highly explosive hydrogen-air atmospheres in storage magazines and warehouses.

Finely divided aluminum (Al) (particle size usually (16 microns) also reacts with moisture to produce  $\rm H_2$ , but at a much slower rate than Mg. Aluminum powder oxidizes very slowly because of the dense protective oxide on its surface. Magnesium, however, is more reactive to water because its oxide coating is porous and nonprotective.

However, one of the most important factors contributing to the reaction of Mg and Al with water is the solubilities of their oxides in acidic and basic mediums created by the oxidants present in the compositions (refs l and 2). Magnesium oxide is readily soluble in acids, but insoluble in bases. Aluminum oxide, however, is soluble in both acids and bases. Consequently, if one uses alkali or alkaline metal nitrates, which are commonly used as pyrotechnic oxidants, the nitrates in the presence of moisture produce  $\rm H_2$  which reacts in part to reduce the nitrates to ammonia (NH<sub>3</sub>) gas. This creates a basic medium which in Mg compositions has no effect on the controlling Mg(OH) $_2$  coating, while in Al compositions results in a dissolution of the protective  $\rm Al(OH_3)$  coating. Consequently, in the Al case, considerable self-heating can occur, possibly leading to explosion.

The purpose of this study was to find a coating material, and a method of applying the coating, to protect finely divided Mg and Al from attack by water vapor. The amount of coating must be small so as not to detract from the performance characteristics of the pyrotechnic composition using the coated fuel.

#### **EXPERIMENTAL PROCEDURE**

The experimental method used to measure the reactivities of coated and uncoated Mg to water consisted of placing the samples in a small 57-cm $^3$  bomb immersed in a constant temperature bath at 62°C. Humidities of 50 and 70% RH were established in the bomb using saturated aqueous salt solutions. The  $\rm H_2$  pressure generated in the bomb was measured using a strain gauge transducer and a visicorder time base recorder.

#### **DISCUSSION**

# Desired Properties of the Coating Materials

The following factors must be considered in choosing a coating for metals (or other ingredients) used in pyrotechnic compositions:

1. The materials must be easily applied. One of the simplest methods of coating finely divided metals is by immersing them in a solution containing a given quantity of coatant and then stirring the mixture constantly until the solvent evaporates, leaving the coatant on the metal.

Another highly desirable method of easily coating the metal is to have a coatant material which will react with the -OH groups on the metal surface to form a strongly bound and impervious coating.

- 2. The amount of coatant used must be small. This is important so that the coating does not reduce the energy output of the system.
- 3. The coating material must produce a free flowing powder, not a sticky mass of agglomerated metal particles.
- 4. The coatant must not reduce the reactivity of the metal. It should decompose or preferably react with the pyrotechnic oxidants used in the composition so as not to interfere with the metal oxidation process.
- 5. The material used to coat the metal should produce a hard surface. This is an important factor since pyrotechnic processing procedures may damage or abrade the coating surface.

# Organic Titanates as Coatants

STATES OF THE PROPERTY OF THE

A study was conducted to reduce H<sub>2</sub> gassing by coating the surface of magnesium particles using organic titanates developed by Kenrich Petrochemicals, Inc. of Bayonne, NJ. Titanates are very large organic molecules (fig. 1) that react with the protons on the surface of Mg and Al to form an organic titanium monomolecular layer. The reaction producing the protective titanium-organic layer is shown in figure 2.

There are a large number of organic titanates that were developed to render materials hydrophobic, act as crosslinking agents in certain organic, polymer systems, reduce the viscosities of filler systems, etc. Another advantage of organic titanates is that only 0.1% by weight is required. This is important since the titanate additive is used in such small quantities that it detracts from the total energy of the pyrotechnic system.

It was found that the titanates used (LICA-12 and 38) did not significantly reduce the reaction of Mg with water vapor as shown in figure 3. However, it was

discovered that the titanates rendered the Mg very hydrophobic to liquid water. Another important finding was that the titanates produced up to a three-fold reduction in the viscosity of Mg slurry mixes similar to those used in extruding Mg compositions. This is an important finding because it would allow processors to use less binder materials thereby increasing energy outputs and reducing composition costs.

An electron microscope picture of 200/325 atomized Mg is shown in figure 4. The material consists of a large particle size distribution of spherical particles apparently clumped together, perhaps by electrostatic forces. When 1% of a titanate (in this case KR-TTS) was added to the same Mg material, it was found that the particles were somewhat coated and appeared to be more distinct and separated from each other (fig. 5). However, the hydrogen gassing experiments clearly showed that the titanate had virtually no effect on reducing attack of water vapor.

# Microcrystalline Wax as a Coatant

The possibility of reducing the H<sub>2</sub> gassing of Mg by the use of microcrystalline wax was investigated. A sample of 23 micron, atomized Mg was coated with 5% by weight of microcrystalline wax no. 1135/15W manufactured by the Ross Co., Inc, and an electron micrograph was obtained (fig. 6). It was found that the wax seemingly coated the Mg very effectively, but at magnifications of 1900X, it was found that many small areas of Mg were uncoated.

It was further found that the wax coated Mg, instead of producing less gas, produced more gas (fig. 7). This increase in pressure can only be accounted for by loss of volatiles from the wax.

# Elvax as a Coatant

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It was suggested by several knowledgable authorities in the field of coatings, that Elvax-360 might be a good coating for powdered Mg and Al. Elvax is the product name of an ethylene/vinyl acetate copolymer manufactured by the DuPont Corporation. This material has a highly desirable tensile strength of 3800 psi and a Shore A-2 Durometer hardness of 85.

The Elvax coating was applied in the laboratory by simply stirring Mg powder in a solution containing 5% of the polymer in toluene. The mixture was constantly stirred while the toluene evaporated. A very evenly coated, free flowing powder was obtained.

An electron photomicrograph of the coating obtained with 5% Elvax-360 is shown in figure 8. One of the most outstanding features noted was that the particles were separated and not clumped together as was the case when other coatants were used. Another outstanding finding was that the Elvax-360 formed a complete coating around nearly all of the particles.

Electron microscope pictures of magnesium (200/325)/Teflon compositions coated with 5% Elvax (fig. 9) also showed that Elvax formed an excellent coating around both the magnesium and TFE (irregular shaped chunks seen in micrographs).

Unfortunately, time was not available to determine the  $\rm H_2$  gassing of the Elvax coated Mg powder. However, a curve was obtained for a pellet of atomized Mg which was dipped into a 10% Elvax-360 solution. This  $\rm H_2$  gassing curve (fig. 10) shows that the Elvax significantly reduced the reaction of  $\rm H_2O$  vapor with the Mg.

One of the most undesirable properties of Elvax-360 is its lack of solubility in common organic solvents. Elvax is only soluble in toluene and clorinated solvents. Use of these solvents are frowned upon because of their toxicities. Consequently, application methods must be used to protect processors from the solvent vapors.

Another method of safely applying the Elvax is by a hot melt process. This process is now being investigated at ARDEC.

# Effects of Elvax on the Performance Characteristics of Mg/Teflon Flares

A number of experiments were conducted to determine if Elvax-360 would have any adverse effects on the performance characteristics of Mg/Teflon flares. A number of small flares were made having an inner diameter of 0.5 inches and length of 3 inches. The results of burning these flares are presented in table l.

It was found that the Mg/Teflon flares containing 5% Elvax-360 had faster burning rates but equal or greater efficiencies (energy/gram of composition) compared to the flares containing Hycar and Viton-A. The increased burning rates of the flares containing Elvax can easily be reduced by adjusting the particle sizes of the ingredients. The important finding was that the Elvax compositions gave equivalent effeciencies and rise times compared to those produced by the standard Hycar and Viton binder systems.

# Crush Strength of Mg/Teflon/Elvax-360 Pellets

The crush strengths of 3/8-inch diameter by 1/2-inch long pellets of Mg/Teflon compositions containing Elvax-360 were compared to those obtained using other binders or additives (table 2). The Elvax pellets had a crush strength more than double the strengths of the Hycar and Viton systems. This is an important property for general handling and ability of the composition to withstand various setback forces.

# Effects of Elvax on the Sensitivities of Pyrotechnic Compositions

One of the important aspects to consider when developing any new pyrotechnic composition is its sensitivity to impact. The effects of Elvax-360 on the impact sensitivities of two important pyro compositions used by the U.S. Army is shown in table 3.

Coating the total composition with 5% Elvax significantly reduced the impact sensitivity (22 to more than 240 cm) of the M21 flash composition, while it had a small, but desirable effect of decreasing the sensitivity of the M119 scratcher composition used in Army igniter systems. It is believed that the Elvax acts to separate the pyrotechnic ingredients to reduce their sensitivities and general reactivities.

#### **CONCLUSIONS**

The conclusions arrived at in this study are summarized as follows:

# Organic titanates

- 1. Did not coat Mg particles efficiently
- 2. Rendered Mg hydrophobic but permeable to water vapor
- 3. Significantly reduced viscosity of flare/binder systems

#### Microcrystalline wax

- 1. No significant reduction in hydrogen gassing
- Coating soft and easily damaged in pyrotechnic handling and processing procedures

# Elvax-360

- 1. Coats Mg very efficiently
- 2. Produces individual particles and free flowing powder
- 3. Significantly reduces hydrogen gassing
- 4. Gives comparable performance characteristics to present flare systems using Hycar and Viton-A binders
- 5. Produces greater pellet strengths than those possible using present binders

6. Renders compositions less impact sensitive than conventional binders

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- 2. Jackson, B., Taylor, F.R., Motto, R., and Kaye, S.M., "Substitution of Aluminum for Magnesium as a Fuel in Flares," Technical Report 4704, Picatinny Arsenal, NJ, Jan 1975, pp 8-10.

Table 1. Performance characteristics of Mg/Teflon flares containing Elvax-360

Composition		Mean burning rate (in./sec)	Efficiency
Mg/Teflon +9% Mg/Teflon +5% Mg/Teflon +5%	Hycar	0.090 0.095 0.143	112 130 132

NOTE:

Flares were 0.5 in. diameter and 3 in. long

Viton-A, a DuPont fluoroelastomer

Hycar rubber, a Goodrich acrylonitrile elastomer

Table 2. Crush test results for 3/8-inch diameter by 1/2-inch long pellets of Mg/Teflon composition containing various binders

Composition	Tensile strength (psi)
18% Viton, no titanate	4() 2
18% Viton, 0.3% LICA 12	47()
14% Viton, 0.3% LICA 12	492
9% Viton, 0.3% LICA 12	574
5% Hycar, no titanate	534
5% Elvax, no titanate	1124

NOTE:

Manfacuturer's tensile strength data:

Viton = 2000 psi Elvax-360 = 3800 psi Hycar > 1500 psi

# Table 3. Effects of Elvax coating on sensitivities of pyrotechnic compositions

# M21 flash composition

62% Ba( $NO_3$ )<sub>2</sub>, 23% A1, 15% S Impact = 22 cm using 2.5 kg weight

Coated with 5% Elvax-360 Impact = >240 cm

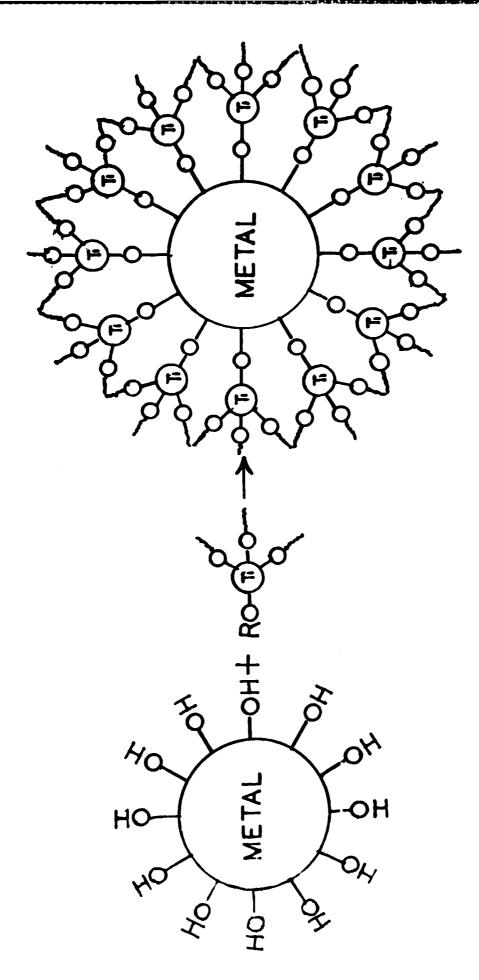
# M119 scratcher composition

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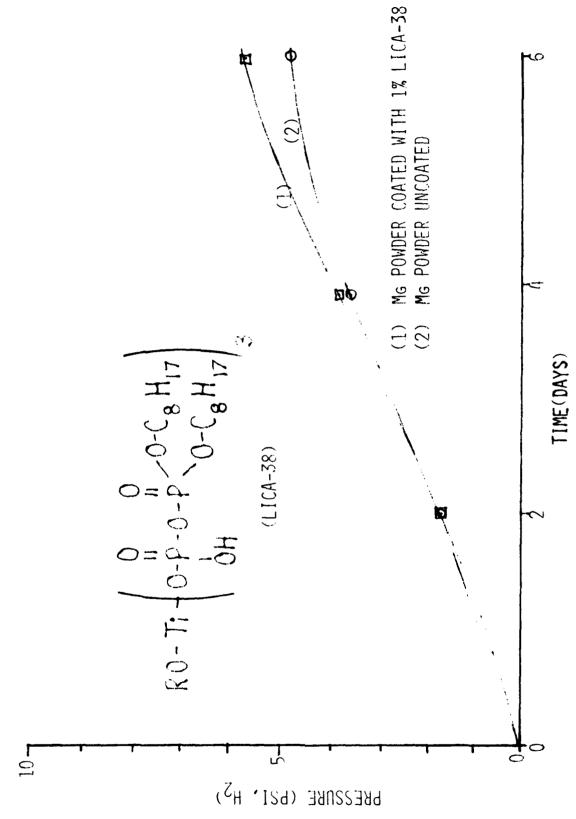
52% KClO $_3$ , 31% Sb $_2$ S $_3$ , 17% dextrin Impact = <14 cm

Coated with 5% Elvax-360 Impact = 16 cm

$\begin{array}{c} C_{17} H_{35} \\ C = 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	typical monoalkoxy triorganofunctional titanate coupling agents
Co Hiz P=0 P=0 P=0 P=0 Co Hiz	Figure 1. Two typical monoalkoxy tri
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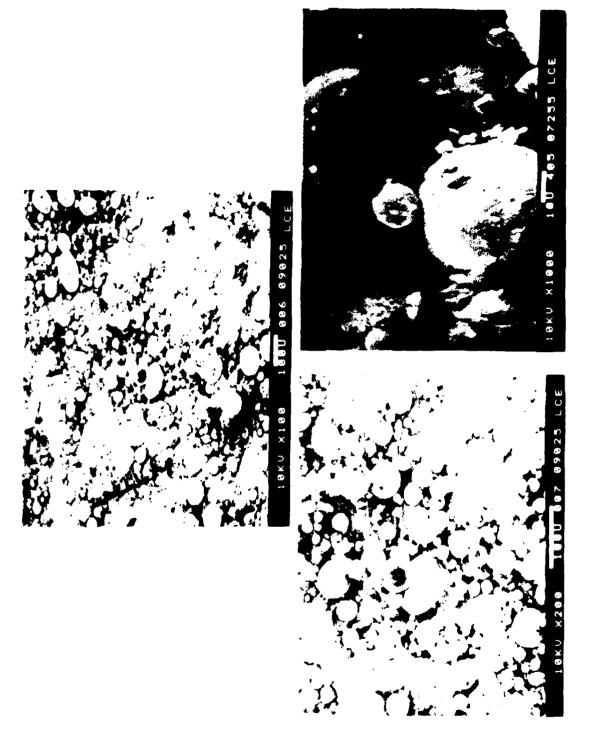


Mechanism by which metal is rendered hydrophobic by an organic function. Figure 2.



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Hydrogen pressure developed by the reaction of water vapor with uncoated and titanate (LICA-38) coated magnesium Figure 3.



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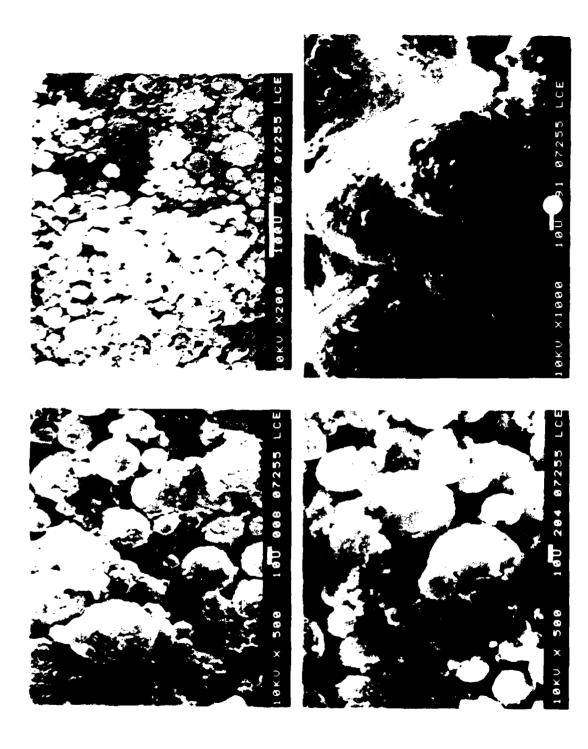
Electron microscope pictures of atomized magnesium (200/325) as received from manufacturer Figure 4.



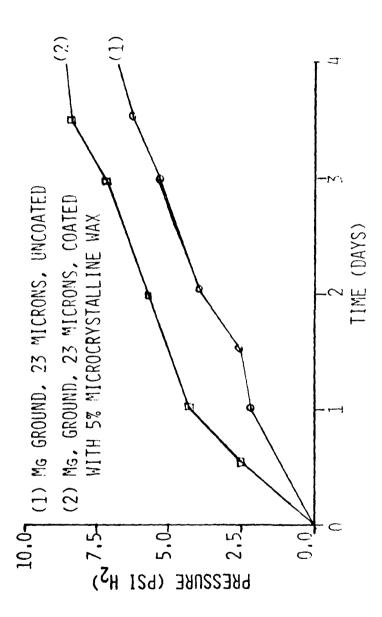




Electron microscope pictures atomized (200/325) coated with 1% KR-TTS titanate Figure 5.



Electron microscope pictures of atomized magnesium (200/325) coated with 5% microcrystalline wax Figure 6.

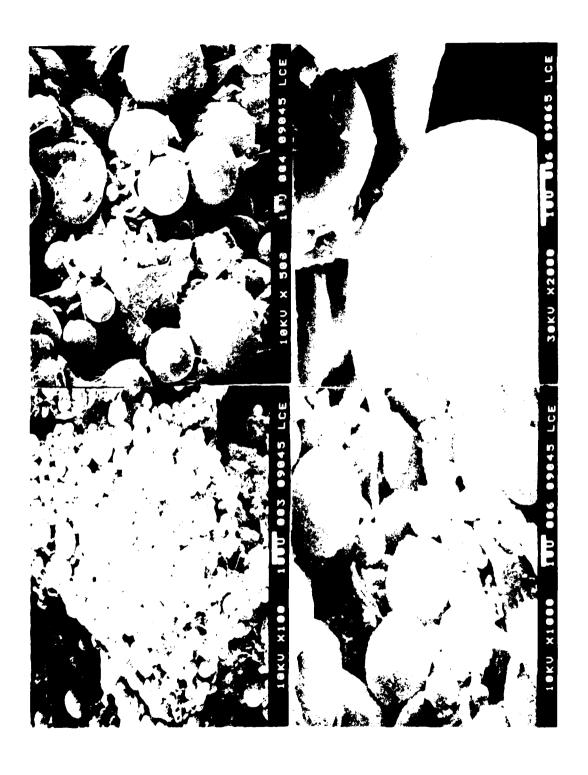


NOTE: % = 23 microns, ground, T = 62°C, RH = 50%

Hydrogen pressure developed by the reaction of magnesium powder with water vapor Figure 7.

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Electron microscope pictures of atomized magnesium (200/325) coated with 5% Elvax-360 Figure 8.



Electron microscope pictures of atomized magnesium (200/325)/Teflon compositions coated with 5% Elvax-360 Figure 9.

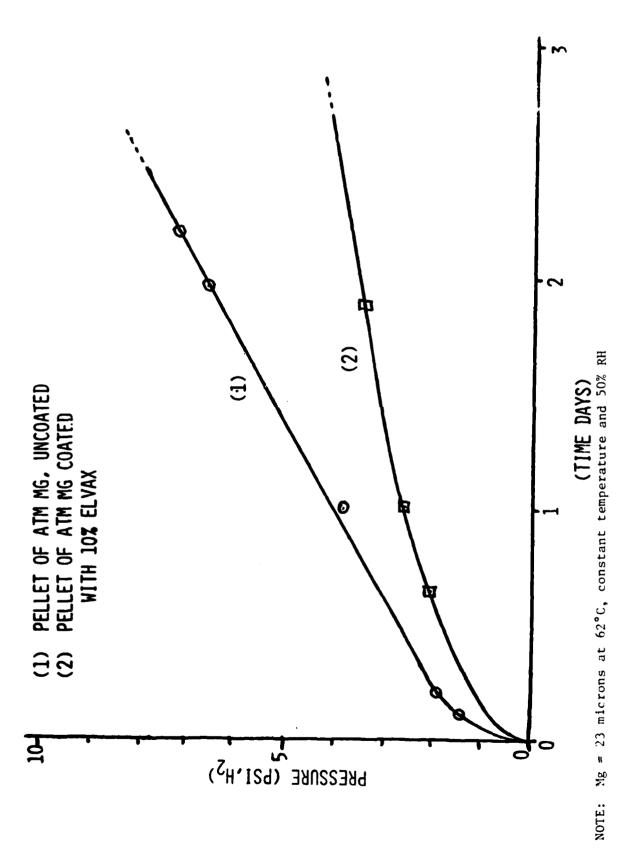


Figure 10. Hydrogen pressure developed by the reaction of pelletized magnesium with water vapor

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